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B3V 10****(56) Documents cited****GB 1426853****US 4070197A****US 3079273A****US 2938807A****US 2431326A****US 2319323A****(58) Field of search
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carbide**

(57) A method of joining together at least two silicon carbide elements, e.g. in forming a heat exchanger, comprises subjecting to sufficiently non-oxidizing atmosphere and sufficiently high temperature, material placed in space between said element, said material comprising silicon carbide particles, carbon and/or a precursor of carbon, and silicon, such that said material forms a joint joining together said at least two silicon carbide elements. At least one of the elements may contain silicon.

SPECIFICATION

Method for joining siliconized silicon carbide elements and resulting product

- 5 The invention relates to a method of forming refractory articles by joining together two or more parts. More specifically, the invention is concerned with a method of joining dense
10 siliconized silicon carbide parts through a siliconized silicon carbide bonding layer.

- The following U.S. Patents are representative of the most relevant prior art known to the Applicant at the time of filing the U.S.
15 application on which the present U.K. application is based:

UNITED STATES PATENTS

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|----|-----------|---------------|--------------------|
| | 2,319,323 | May 18, 1943 | A. H. Heyroth (I) |
| 20 | 2,431,326 | Nov. 25, 1947 | A. H. Heyroth (II) |
| | 2,938,807 | May 31, 1960 | J. C. Andersen |
| | 2,964,823 | Dec. 20, 1960 | J. I. Fredriksson |
| | 3,079,273 | Feb. 26, 1963 | J. R. Johnson |
| | 4,070,197 | Jan. 24, 1978 | S. H. Coes |

- 25 The present invention has for its main objective, the permanent bonding together of previously highly densified silicon carbide parts or elements to form a finished product of complex configuration, e.g. a heat exchanger.
30 The terms "siliconized silicon carbide" as used hereinafter means silicon carbide containing some amount of silicon regardless of how the silicon containing silicon carbide
35 body or part was fabricated.

- Highly dense silicon containing articles can be made as taught by the Heyroth (II) reference. Accordingly, a porous carbon shape is first formed by shaping a mixture of carbon
40 powder and a binder. The carbon skeleton is then subjected to elemental silicon at a temperature well above the melting point of the silicon. The latter permeates the carbon skeleton and forms silicon carbide in situ. The
45 silicon may be introduced into the carbon shape by contacting the latter with molten silicon or it may be exposed to silicon vapors. The resulting product is a highly dense structure made up of silicon carbide, silicon and a
50 very low percentage of pores. The relative amounts of silicon carbide and silicon can be controlled within limits.

- Andersen discloses another method of forming highly dense siliconized silicon carbide.
55 Here granular silicon carbide is mixed with a carbonaceous material such as graphite or amorphous carbon, and a carbonizable material such as an organic polymer which may function as a temporary binder as well as a
60 carbon donor. The mixture is then formed into the desired shape and heated to set and decompose the temporary binder. The porous silicon carbide-carbon body is then fired in the presence of silicon, converting most of the
65 carbon to silicon carbide. The resulting prod-

uct is very dense, having a density of at least 3.0 g/cc, and a free silicon content of below about 5% by weight.

- Still another method of forming highly
70 dense siliconized silicon carbide involves impregnation of porous recrystallized silicon carbide articles made according to Fredriksson. Green silicon carbide shapes are formed by slip casting; the shapes are then fired to
75 recrystallize the silicon carbide. Fredriksson's teachings can be employed to make products with variable degrees of porosity. The fired silicon carbide shapes may then be exposed to silicon to facilitate impregnation.

- 80 While the foregoing methods provide the appropriate materials, the limitation on the degree of complexity of article configuration inherent in these methods, even the Fredriksson slip casting method, is a persistent
85 problem.

- Heyroth (I) describes a method for welding together several silicon carbide parts which could be used to form complex shapes. Silicon carbide parts, which are formed by siliconizing a carbon skeleton essentially as per
90 Heyroth (II), are bonded together by first placing carbon between two or more parts in the form of a paste of flour, carbon, charcoal and casein glue; heating the in place paste to
95 form a carbon skeleton; and, exposing the carbon skeleton to silicon at a temperature of at least 1800°C. The silicon impregnates the carbon skeleton forming a silicon carbide and silicon weld or joint.

- 100 Another method of joining silicon carbide elements is that of Coes. Gas impermeable hollow silicon carbide articles are formed by slip casting or otherwise creating green silicon carbide parts or elements which are then
105 cemented together with additional silicon carbide slip. The joined elements are then fired in the well known manner, to recrystallize the silicon carbide in the elements per se and in the joint between the elements. This unitary
110 article is then subjected to a silicon atmosphere which deposits sufficient silicon in the structure, including the joint, to render it impervious.

- The Johnson reference is primarily concerned with the fabrication of siliconized silicon carbide articles per se. However, it does teach the welding together of graphite parts or parts formed from a mixture of carbon, a film forming polymer, and powdered, silicon
120 carbide. The welding mixture is also made up of carbon, a film forming polymer, and silicon carbide powder. The welding mixture very effectively bonds to graphite when contacted with the graphite and siliconized. The siliconization causes the production of silicon carbide in the welding mixture per se and in the
125 graphite at the interface of the graphite body and the welding mixture, thus causing an intergrowth of silicon carbide crystals and a
130 good bond. Johnson also teaches the forma-

tion of green parts using the disclosed carbon-polymer-silicon carbide mixture; joining these parts together with a thin layer of the same carbon-polymer-silicon carbide mixture; and, siliconizing the assembled green composite structure.

In the present invention, e.g. previously densified siliconized silicon carbide parts or elements are joined to form complex articles, by a refractory cement which produces a joint at least as strong as the main silicon carbide body.

The refractory cement can be made from fine silicon carbide and carbon (per se or a carbonizable material); whenever the term carbon is used herein, it is meant to include both carbon per se or a carbonizable material unless otherwise specified. The cement is placed between the gap formed by two silicon carbide elements and siliconized at a temperature at least high enough to melt the silicon metal e.g. 1700 to 2300°C, causing it to impregnate the silicon carbide-carbon cement, where the silicon reacts with a substantial amount of carbon to form silicon carbide. Reference should be made to U.S. Patent No. 4,019,913 issued to Weaver et al, the contents of which are hereby incorporated herein.

The refractory cement may be in the form of a paste in which case it is troweled or injected between the space formed by the siliconized silicon carbide parts, or it may be in the form of a casting slip of the type taught by Fredriksson in U.S. Patent No. 2,964,823, whose contents are hereby incorporated herein. In both cases the placed cement is dried if originally a slip or dried and heat treated at a low temperature to cure any temporary binder and/or carbonizable organic material.

While the following discussions of preferred embodiments are directed specifically to the joining together of siliconized silicon carbide elements, it should be understood that the present method is also applicable to the cementing together of parts which are made from sintered or reaction bonded silicon carbide.

The particle or grain size of the silicon carbide based refractory cement can be approximately the same as the particle or grain size of the silicon carbide in the densified silicon carbide parts which are to be joined. For optimum strength it is desirable that the cement (and the parts to be joined) be made up of approximately 50% by weight of silicon carbide having a particle size of about 0.1 to 8.0 microns and approximately 50% by weight of silicon carbide having a particle size of about 30 to 170 microns. However, it is advantageous in some respects to use a finer coarse fraction of silicon carbide in the cement e.g. of the order of about 10 to 20 microns. This particle size of the coarse fraction is more desirable if the cement is applied in the form of a casting slip.

Where optimum strength and impermeability is required both the parts to be assembled and the final cement should have as little porosity as possible. A maximum porosity of about 5% is preferred and produces a very high strength, impermeable material in both the finished article and the joints between the parts assembled to form that article.

75 Example

A densified siliconized silicon carbide piece, measuring 1" × 2" × 3/8" (2.54 cm × 5.08 cm × 0.95 cm), was fabricated in the following manner:

80 A bimodal mixture of silicon carbide was prepared, made up of 48% by weight of 100 mesh and 52% by weight of 3 micron silicon carbide. The 100 mesh refers to silicon carbide particles having a particle size spread of 85 from substantially 30 microns to substantially 170 microns. The two sized silicon carbide powders were blended together with 12.5% by weight of water and 0.5% by weight of sodium silicate. The mixture was rolled in a 90 jar mill for 12 hours thus forming a casting slip of the type described by U.S. Patent No. 2,964,823 issued to J. I. Fredriksson.

The slip was then cast into a porous plaster mold which had a cavity measuring 6" × 6" 95 × 3/8" (15.24 cm × 15.24 cm × 0.95 cm). The piece was air dried at room temperature overnight and then fired to 1970°C in an inert atmosphere, to lightly sinter the piece. After this initial firing, a 1" × 2" × 3/8" 100 (2.54 cm × 5.08 cm × 0.95 cm) piece was then impregnated with a furfuryl alcohol resin solution (Fapreg PS manufactured by the Quaker Oats Co.). The impregnant was freed of solvent and polymerized by heating at 105 90°C for 24 hours, 150°C for 6 hours, and 250°C for 2 hours. The piece was then fired at 2070°C in a sintering furnace in contact with molten silicon metal, all in a nitrogen atmosphere. The molten silicon metal infiltrated the carbon containing piece and reacted 110 with the carbon forming silicon carbide. The remaining voids, about 10%, were filled with silicon metal and had a density of 3.12 g/cm.

The densified siliconized silicon carbide 115 piece was then cut in half with a diamond saw. The two pieces were placed on a graphite plate with the two cut surfaces facing each other and spaced about 0.04 inch (0.01 cm) apart. The pieces were held in place with 120 masking tape placed around the perimeter of the two pieces. The tape also functioned as a dam or retainer for the cement at opposite ends of the space formed by the two pieces. A bond or cement was prepared by mixing 125 44.72 gm of 3 micron silicon carbide, 42.8 gm of (e.g. 220F mesh) silicon carbide, and 15 gm of a 1% sodium silicate-water solution. The 220F mesh refers to silicon carbide particles that will pass through a screen having 130 openings of substantially 66 microns. The

bond was poured into the gap formed by the cut surfaces of the two pieces of densified silicon carbide and masking tape. The bond was allowed to dry at room temperature for 24 hours. The excess bond was trimmed off the top surface so that the bond in the joint was level with the top surfaces of the two pieces. The partially bonded piece was removed from the graphite plate and immersed for 30 minutes in the same furfuryl alcohol resin solution described above. The entire piece was then cured at 250°C for 4 hours causing the resin to cure and carbonize.

A weight of through 28 mesh silicon metal equal to about 60% of the weight of the entire piece, was placed on top of the piece in a level pile. The 28 mesh refers to silicon metal particles that will pass through a screen having openings of substantially 590 microns. The piece was then placed in an induction furnace and heated to about 2070°C and held at that temperature using a nitrogen purge throughout, after which the piece was allowed to cool to room temperature.

Test bars measuring 1/8" × 1/8" × 1" (0.32 cm × 0.32 cm × 2.5 cm) were cut from the finished piece, with the newly formed joint approximately in the middle of the length of each bar. Eight test bars were broken in cross-bending on an Instron tester using a three point-1" (2.5 cm) span bend ring. The average modulus of rupture was 41,165 psi (28.8 kg/mm²). In every case failure was in the body of the test bar and not in the joint.

It should be understood that the foregoing description of the preferred practice of the invention is in no way to be construed as limiting. Other variations within the scope of the appended claims may be apparent or occur to one skilled in the art e.g. densified silicon carbide parts may be joined according to the invention by placing a silicon carbide cement which is free of carbon, in the joint followed by firing at an elevated temperature to more or less sinter the cement. The carbon or carbonizable material may then be introduced and siliconized.

It will be appreciated that the present invention can provide unitary high density siliconized silicon carbide articles formed from two or more already siliconized silicon carbide parts joined together by placing fine, carbon containing, silicon carbide between the parts or elements and siliconizing to form a bonded joint. The joints per se can be of a density equal to or even greater than that of the joined parts and possess strength properties at least equal to those of the parts or elements.

CLAIMS

1. A method of joining together at least two silicon carbide elements, comprising subjecting to sufficiently non-oxidizing atmosphere and sufficiently high temperature, ma-

terial placed in space between said elements, said material comprising silicon carbide particles, carbon and/or a precursor of carbon, and silicon, such that said material forms a joint joining together said at least two silicon carbide elements.

2. A method as claimed in claim 1, wherein said non-oxidizing atmosphere comprises an inert gas.

3. A method as claimed in claim 2, wherein said inert gas comprises nitrogen gas.

4. A method as claimed in any one of claims 1 to 3, wherein said temperature comprises any temperature in the range substantially 1700 to substantially 2300°C.

5. A method as claimed in any one of claims 1 to 4, wherein at least one said element has been previously densified.

6. A method as claimed in any one of claims 1 to 5, wherein at least one said element is siliconized silicon carbide.

7. A method as claimed in any one of claims 1 to 6, wherein at least one said element is reaction bonded silicon carbide.

8. A method as claimed in any one of claims 1 to 7, wherein at least one said element is sintered silicon carbide.

9. A method as claimed in any one of claims 1 to 8, wherein in said space at least a portion of said material was placed by trowelling or the like.

10. A method as claimed in any one of claims 1 to 9, wherein in said space at least a portion of said material was placed by injection or the like.

11. A method as claimed in any one of claims 1 to 10, wherein in said space at least a portion of said material was placed as a cement or the like.

12. A method as claimed in any one of claims 1 to 11, wherein in said space at least a portion of said material was placed as a casting slip.

13. A method as claimed in any one of claims 1 to 12, wherein at least a portion of said placed material is dried material.

14. A method as claimed in any one of claims 1 to 13, wherein at least a portion of said placed material is sintered material.

15. A method as claimed in any one of claims 1 to 14, wherein in said placed material said silicon carbide particles have at least one particle size in the range substantially 0.1 to substantially 8.0 microns.

16. A method as claimed in any one of claims 1 to 15, wherein in said placed material said silicon carbide particles have at least one particle size in the range substantially 10 to substantially 20 microns.

17. A method as claimed in any one of claims 1 to 16, wherein in said placed material said silicon carbide particles have at least one particle size in the range substantially 30 to substantially 170 microns.

18. A method as claimed in any one of

claims 1 to 17, when according to claim 15, wherein in said placed material there is up to substantially 50% by weight of said at least one particle size in the range substantially 0.1 to substantially 8.0 microns.

19. A method as claimed in any one of claims 1 to 18, when according to claim 17, wherein in said placed material there is up to substantially 50% by weight of said at least one particle size in the range substantially 30 to substantially 170 microns.

20. A method as claimed in any one of claims 1 to 19, wherein at least a portion of said carbon is present in said placed material.

21. A method as claimed in any one of claims 1 to 20, wherein at least a portion of said carbon precursor is present in said placed material.

22. A method as claimed in claim 21, wherein said carbon precursor comprises cured organic material.

23. A method as claimed in claim 22, wherein said cured organic material has been cured by application of at least heat thereto.

24. A method as claimed in claim 22 or 23, wherein said cured organic material is derived from a composition comprising furfuryl alcohol resin.

25. A method as claimed in any one of claims 1 to 24, wherein said carbon and/or carbon precursor in said placed material was incorporated therein by impregnation.

26. A method as claimed in any one of claims 1 to 25, wherein said silicon in said placed material was incorporated therein from molten silicon.

27. A method as claimed in any one of claims 1 to 26, wherein, in said subjecting, said silicon in said placed material reacts with a substantial amount of said carbon or carbon precursor.

28. A method as claimed in any one of claims 1 to 27, wherein said joined together elements and said joint have a porosity of at most substantially 5%.

29. A method as claimed in any one of claims 1 to 28, wherein said joint has a density of at least substantially equal to that of at least one said element.

30. A method as claimed in any one of claims 1 to 29, wherein said joint has a strength at least substantially equal to the strength of at least one said element.

31. A method as claimed in claim 1, substantially as described in the Example.

32. A composite, comprising at least two silicon carbide elements joined together by at least one siliconized carbide joint, said composite optionally having a porosity of at most 5%.

33. A composite as claimed in claim 32, when prepared by a method as claimed in any one of claims 1 to 31.

34. A composite as claimed in claim 32 or 33, wherein said composite is an article.

35. A composite as claimed in claim 34, wherein said article has at least one complex configuration.

36. A composite as claimed in claim 34 or 35, wherein said article is a heat exchanger, a component of a heat exchanger, or the like.

37. A method of permanently joining two or more previously densified silicon carbide elements, comprising the steps of:

locating said densified silicon carbide elements in close proximity to each other so as to form a gap therebetween;

placing silicon carbide powder and carbon in said gap to form a joint;

impregnating the silicon carbide powder and carbon in the gap with molten silicon in a non-oxidizing atmosphere at a temperature sufficiently high to cause a substantial amount of silicon carbide to be formed between the molten silicon and said carbon.

38. The method of claim 37, wherein the silicon carbide powder is placed in said gap in the form of a casting slip, said slip is dried, and carbon is introduced into said silicon carbide joint in the form of a carbonizable organic material, the silicon is caused to impregnate the joint at a temperature of about 1700°C to about 2300°C, and wherein said densified silicon carbide is siliconized silicon carbide.

39. The method of claim 38, wherein the silicon carbide in said casting slip is about 50% by weight of silicon carbide having a particle size of about from 0.1 to 8 microns and about 50% by weight of silicon carbide having a particle size of from about 30 to 170 microns, and the carbonizable organic material is introduced into the unfired joint by impregnation.

40. A high density siliconized silicon carbide article made up of two or more elements bonded together by siliconized silicon carbide joints wherein said elements and said joints have a maximum of 5% porosity.

41. The siliconized silicon carbide article of claims 40, wherein the silicon carbide powder used to form said elements and said joint is bimodal and made up of about 50% by weight of silicon carbide having a particle size of from about 0.1 to 8 microns, and 50% by weight of silicon carbide having a particle size of from about 30 to 170 microns.

42. The siliconized silicon carbide article of claim 41, wherein the strength of said joints is at least approximately equal to the strength of said elements.